Investigation of Acrylic Acid Polymerization in Novel Two-Dimensional Molecular Space with Regular Amino Groups of Layered Aminopropylsilica

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Acrylic acid was used to investigate the capabilities of novel two-dimensional molecular space with regular amino groups (layered aminopropylsilica, ATMS-DS) on influencing and controlling molecular reaction processes. The acrylic acid was regularly fixed in the layer structure of layered aminopropylsilica through the formation of amide between carboxyl of acrylic acid and amino groups of layered aminopropylsilica. The acrylic acid regularly fixed in layered aminopropylsilica was completely polymerized to form a novel organic−inorganic nanocomposite material named as layered polyacrylamidepropylsilica (ATMS-PAA) with monolayers of polyacrylamide in layer space of layered aminopropylsilica without initiator after being heated at 100 °C for 24 h. It was found that the polymerization of acrylic acid was facilitated in the novel two-dimensional molecular space with regular amino groups compared with free space. The polymeric structure of ATMS-PAA was also found to be decided by the regular structure of layered aminopropylsilica. The novel two-dimensional molecular space with regular amino groups in structure showed a potential of influencing and controlling molecular reaction processes. The formation of a novel hybrid organic−inorganic nanocomposite material (layered polyacrylamidepropylsilica) is also interesting for the research of polymer nanocomposite materials.

Introduction

Layered materials, such as clay minerals and layered double hydroxides (LDHs), have been investigated extensively as nanospace materials, as they provide a stable two-dimensional nanospace for chemical processes.[1−44]A variety of molecules can be intercalated into the two-dimensional interlayer space of layered materials. Specifically, the inser-

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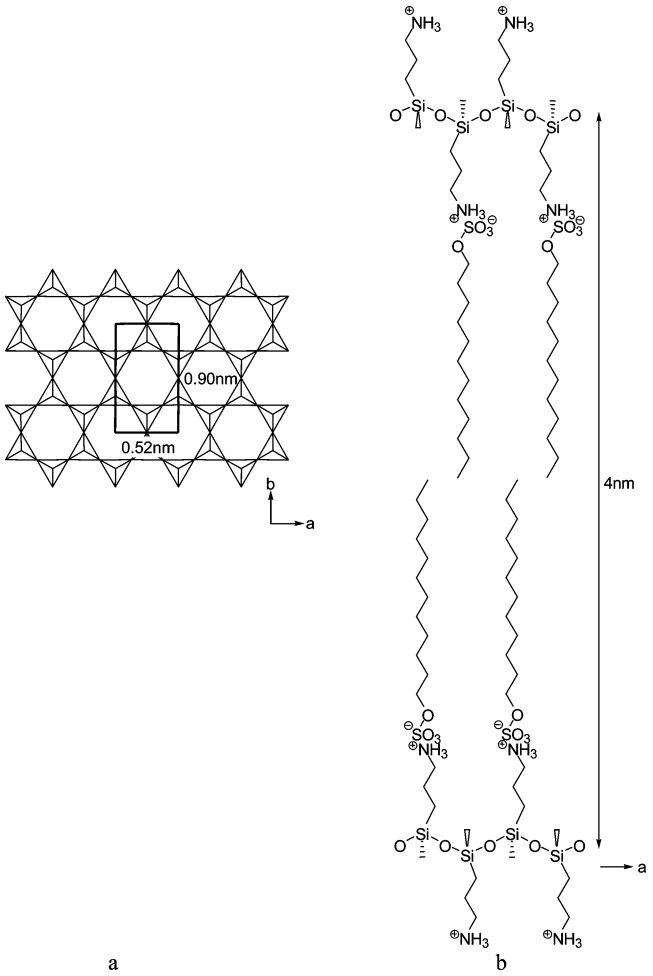
tion of functional molecules is of great interest for the physical chemistry,[5−18] catalysis,[19−21] polymer science,[22−33]and biochemistry.[34−36] The two-dimensional layer structure of layered materials is expandable with the size of the intercalated molecule. The intercalated molecules only can form monolayers or bilayers in the interlayer space of layered materials independent of molecular size, as a result of the interaction between the layer plate and molecules. Some novel chemical and physical properties can be obtained in two-dimensional layer spaces that are different from the macroscopic space.[37−44] Thus, two-dimensional layered materials are promising materials for influencing and controlling molecular reaction processes in two-dimensional layer spaces.

However, it is difficult to influence and control molecular reaction processes in the interlayer space utilizing the current layered materials because of lack of functional properties and unchangeable layer structure. However, much research has been devoted to modify the inorganic layered materials with organic molecules to obtain the functional molecular space. Unfixed and lack of regular arrangement of organic molecules in layer space confined the further application of layered materials.

Previously, we reported a novel two-dimensional layered aminopropylsilica ($C_{12}H_{25}OSO_3^-/NH_3^+C_3H_6SiO_{1.5}$, ATMS-DS) with regular amino groups in layer structure.[45] The layered aminopropylsilica was synthesized using 3-aminopropyltrimethoxysilane (ATMS) templated with anionic surfactant (sodium dodecyl sulfate, SDS) under acidic conditions. The inorganic part of layered ATMS-DS was a highly crystalline Si−O hexagonal sheet as illustrated in Scheme 1a. The lattice parameters of the *a*- and *b*-axes were found to be 0.52 nm and 0.90 nm, respectively. The amino groups were alternately arranged on both sides of the sheet as illustrated in Scheme 1b. The molecular distance of the amino groups from each other on the same side of one sheet is about 0.52 nm. The layered structure of layered aminopropylsilica was retained after the removal of the surfactant using other anions.[45] The layered ATMS-DS with regular amino groups exhibited a stable layer structure and better intercalation response. The better X-ray diffraction (XRD) responses of various intercalation precipitates of layered aminopropylsilica were obtained. The better intercalation behaviors demonstrated the high regular arrangement of propylamine groups in the layer structure of layered aminopropylsilica. We also have developed a novel two-dimensional molecular space material with regular double bonds

Scheme 1. Schematic Illustrations of the Layered Aminopropylsilica[a]



[a] (a) Top view of the Si−O hexagonal sheet; (b) vertical cross-section view of ATMS-DS.

(layered acrylamidephenylsilica) through hybridizing double bonds in the layer structure of layered aminophenylsilica.[46,47] The layered aminophenylsilica with phenylamine groups has different reaction properties from those of layered aminopropylsilica with propylamine groups. The carboxyl of acrylic acid can immediately react with phenylamine groups regularly arranged in layered aminophenylsilica to form layered acrylamidephenylsilica with regular double bonds at room temperature.

Functional two-dimensional molecular spaces can be obtained as a result of the geometrical and chemical properties of organic groups regularly arranged in a layer structure. Perhaps, the molecular reaction processes can be influenced and controlled in the two-dimensional molecular spaces by utilization of the interaction between organic groups regularly arranged in layer structure and guest molecules. Thus it is very interesting to investigate the capabilities of two-dimensional molecular space materials with regular organic groups on influencing and controlling molecular reaction processes.

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In this research, acrylic acid was used to investigate the capabilities of two-dimensional molecular space of layered aminopropylsilica with regular amino groups on influencing and controlling molecular reaction processes. Layered aminopropylsilica was selected to use in this research, because linear propylamine groups regularly arranged in layer structure of layered aminopropylsilica is propitious to control molecular structure of linear acrylic acid. Only the polymerization of acrylate,[22−24] vinyl benzene sulfonate,[25,26] sulfopropyl methacrylate,[28]and aniline sulfonic acid[32,33] in the inorganic layered materials has been investigated as organic−inorganic nanocomposite materials until now. Perhaps the polymerization of acrylic acid can be influenced and controlled by the geometrical and chemical properties of amino groups regularly arranged in layer structure of layered aminopropylsilica. This research attempted to find and prove the potential of novel two-dimensional layered molecular space with regular organic groups on influencing and controlling the molecular reaction processes. The formation of a novel hybrid organic−inorganic nanocomposite material (layered polyacrylamidepropylsilica) is also interesting for the research of polymer nanocomposite materials.

Experimental Section

ATMS and SDS were purchased from the Aldrich Chemical Co. and used as received. The layered aminopropylsilica was synthesized by the very slow titration of hydrochloric acid (0.5 mol·dm^{-3}) into a mixture of 0.5 cm^3 of 97% ATMS (2.78mmol), 0.84 g of SDS (2.92 mmol), and 15 cm^3 of deionized water with stirring at room temperature for 2 weeks to complete the sol−gel process, and the pH value was controlled to be between 2 and 3 as described previously.[45] The white precipitates (ATMS-DS) were filtered and washed with deionized water and ethanol and then dried in vacuum.

The reaction of layered aminopropylsilica with acrylic acid is described as below: 0.6 g of ATMS-DS was added into rockered flask with 15 mL of acrylic acid (98%, purchased from the Aldrich Chemical Co.), and then the mixture was heated at 60 °C and 100 °C under stirring, respectively. The precipitates which became light yellow from white were filtered and washed with deionized water and then dried in a vacuum.

XRD data on the powder samples were recorded with an X-ray diffractometer (Rigaku, D\max-2550) using Cu Kα radiation (0.1541 nm) under the conditions of 40 kV and 30 mA.

The ^{13}C NMR spectrum was recorded on a Bruker AV500 spectrometer operating at 125.77 MHz with $CDCl_3$ as an internal standard. The ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker MSL-300WB (7.05-T) spectrometer. The ^{13}C CP/MAS NMR spectra were obtained at 100.61 MHz. Chemical shifts for ^{13}C NMR were referenced to tetramethylsilane (TMS) at 0 ppm.

Fourier transform infrared (FTIR) spectra were obtained by using an "Avatar 370" spectrophotometer of Nicolet, and the preparation of the samples consisted of dispersing and gently grinding the powder in KBr.

Chemical analyses were performed by elementary organic microanalysis for C, N, and S in a "VerioEL III" element analyzer.

Results and Discussion

Acrylic acid was used to investigate the capabilities of two-dimensional molecular space with regular amino groups (layered aminopropylsilica) on influencing and controlling molecular reaction processes. First, the reaction of layered aminopropylsilica with acrylic acid occurred at 60 °C, due to that any reaction was not observed in the mixture of layered aminopropylsilica and acrylic acid at room temperature. The IR spectra of ATMS-DS and the reactive precipitates (ATMS-AA) between ATMS-DS and acrylic acid heated at 60 °C for 68 h were shown in Figure 1, respectively. The strong stretching vibrations of methylenes of dodecyl sulfate (DS) can be clearly observed at 2800−3000 cm^{-1} in the IR spectrum of ATMS-DS (Figure 1a). The stretching vibrations of methylenes of DS became weaker in the IR spectrum of ATMS-AA formed at 60 °C for 68 h (Figure 1b). A new vibration peak appeared at 1722 cm^{-1} in the IR spectrum of ATMS-AA formed at 60 °C (Figure 1b) compared with ATMS-DS (Figure 1a). The vibration peak at 1722 cm^{-1} was assigned to carbonyl due to formation of amide between amino groups of layered aminopropylsilica and carboxyl of acrylic acid in ATMS-AA formed at 60 °C. It is considered that a part of DS in the two-dimensional interlayer space of ATMS-DS was displaced by acrylic acid and a part of amino groups of layered aminopropylsilica reacted with carboxyl of acrylic acid to form amide in ATMS-AA heated at 60 °C for 68 h. The temperature of 60 °C was obviously too low for the reaction between layered ATMS-DS and acrylic acid.

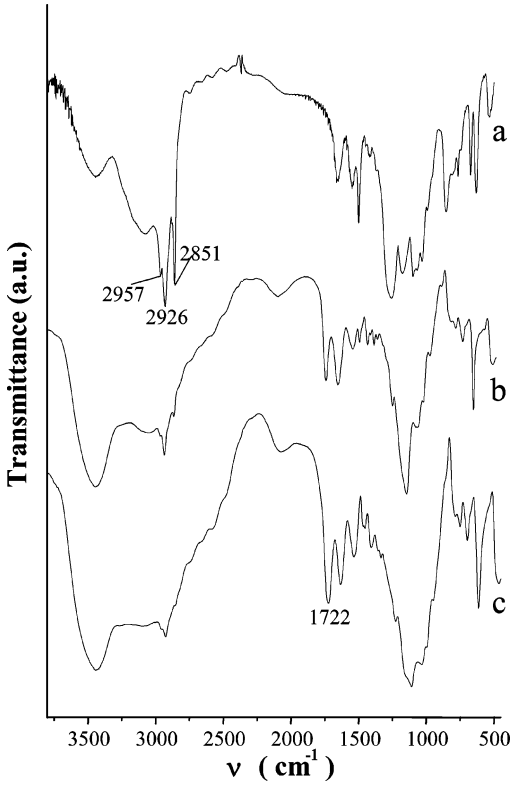


Figure 1. IR spectra of (a) ATMS-DS, (b) ATMS-AA heated at 60 °C for 68 h, and (c) ATMS-AA heated at 100 °C for 24 h.

Then, the reaction of layered aminopropylsilica with acrylic acid occurred at 100 °C. The IR spectrum of reactive precipitates (ATMS-AA) between layered ATMS-DS and acrylic acid heated at 100 °C for 24 h was shown in Figure 1c. The IR spectrum of ATMS-AA showed that the stretching vibrations of methylenes at 2800−3000 cm^{-1} became very weak after 24 h of heating at 100 °C (Figure 1c) compared

with ATMS-DS (Figure 1a). It was not sufficient to conclude the DS in the two-dimensional molecular space of ATMS-DS was completely displaced by the acrylic acid in ATMS-AA after heating 24 h at 100 °C, although propyl groups in layered aminopropylsilica also can arouse the stretching vibrations in IR spectra at a similar position. A stronger carbonyl vibration peak appeared at 1722 cm^{-1} in ATMS-AA heated at 100 °C for 24 h (Figure 1c) compared with heating at 60 °C for 68 h (Figure 1b). The amide was formed between the carboxyl of acrylic acid and amino groups of layered aminopropylsilica heated at 100 °C for 24 h. The polymerization of acrylic acid in layered aminopropylsilica was hardly discussed by the IR spectrum of ATMS-AA formed at 100 °C for 24 h, because the vibration peak of the vinyl groups was covered by the other peaks in layered aminopropylsilica.

The reactive precipitates (ATMS-AA) between ATMS-DS and acrylic acid heated at 100 °C were analyzed with ^{13}C CP/MAS NMR in detail, to investigate the polymerization of acrylic acid in two-dimensional layer space of layered aminopropylsilica. The ^{13}C CP/MAS NMR spectra of ATMS-DS and ATMS-AA heated at 100 °C for 9 and 24 h were shown in Figure 2. The ^{13}C CP/MAS NMR spectrum of ATMS-DS showed a series of resonance peaks assigned to methylenes of DS and propyl groups of layered aminopropylsilica (Figure 2a). The wider low resonance peaks at 9.9, 21.5, and 42.7 ppm were assigned to three carbon species from ATMS ($Si-CH_2-CH_2-CH_2-NH_3^+$) in ATMS-DS. The other sharp resonance peaks were assigned to methylenes of dodecyl sulfate. The resonance peaks at 68.9 and 31.2 ppm were assigned to carbon species connected to the sulfate group and in the middle of alkyl chain in dodecyl sulfate, respectively. No reaction was observed after mixing layered aminopropylsilica with acrylic acid at room temperature, even in the intercalation reaction.

First, the reactive precipitates (ATMS-AA) between ATMS-DS and acrylic acid were analyzed using ^{13}C CP/MAS NMR after heating at 100 °C for 9 h. The ^{13}C CP/MAS NMR spectrum of ATMS-AA heated at 100 °C for 9 h showed eight resonance peaks at 9.9, 21.5, 34, 42.7, 61, 125, 128, and 178.1 ppm referenced to TMS at 0 ppm (Figure 2b). The complex resonance peaks of methylenes of DS observed in ATMS-DS completely disappeared in the ^{13}C CP/MAS NMR spectrum of ATMS-AA heated at 100 °C for 9 h. The DS in the two-dimensional molecular space of ATMS-DS was considered to be completely displaced by the acrylic acid in ATMS-AA. The resonance peaks at 9.9, 21.5, and 42.7 ppm were assigned to three carbon species from ATMS ($Si-CH_2-CH_2-CH_2-NH_3^+$) in ATMS-AA. The resonance peak at 178.1 ppm is different from the ^{13}C NMR resonance peak of carboxyl of acrylic acid which should be obtained at 171.69 ppm. The resonance peak at 178.1 ppm was assigned to the carbonyl of amide formed between amino groups of layered aminopropylsilica and carboxyl of acrylic acid. No resonance peak corresponding to carboxylate was obtained in the ^{13}C CP/MAS NMR spectrum of ATMS-AA heated at 100 °C for 9 h (Figure 2b). The all amino groups of layered aminopropylsilica reacted with carboxyl of acrylic acid to form amide in

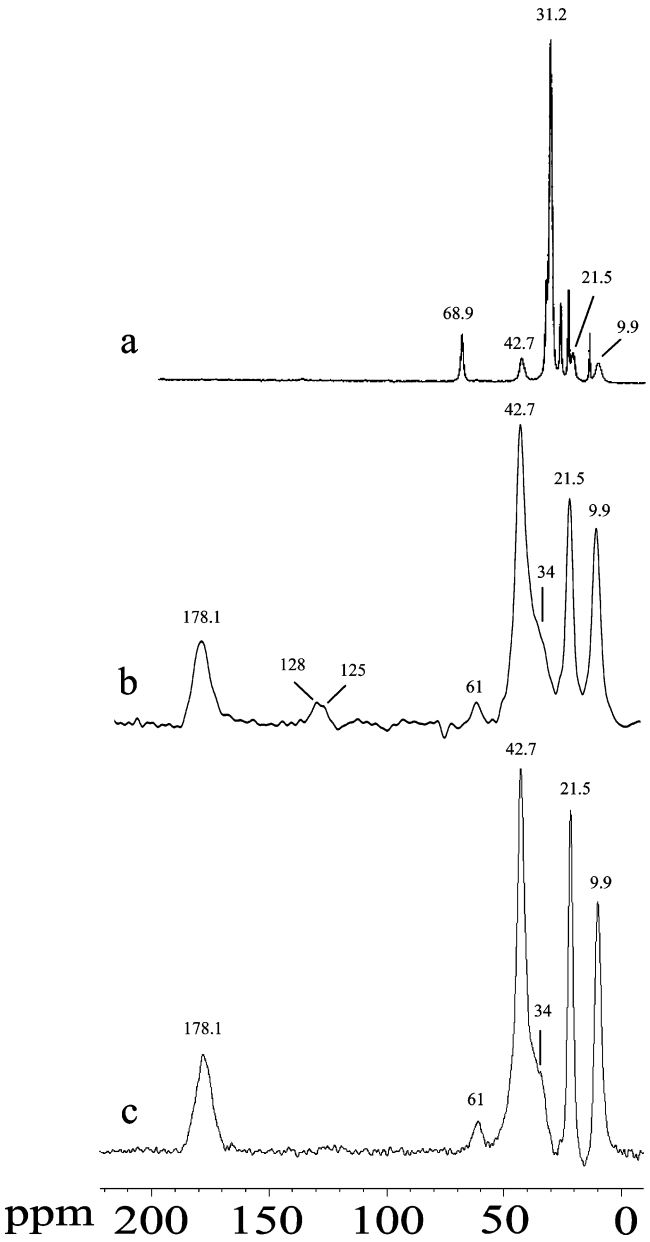


Figure 2. ^{13}C CP/MAS NMR spectra of (a) ATMS-DS, (b) ATMS-AA after heating at 100 °C for 9 h, and (c) ATMS-AA after heating at 100 °C for 24 h.

ATMS-AA heated at 100 °C for 9 h. The acrylic acid was fixed in the layer structure of layered aminopropylsilica through the formation of amide between amino groups of layered aminopropylsilica and carboxyl of acrylic acid. The resonance peaks at 34 and 61 ppm were assigned to the $-CH_2$ and $-CH$ formed from the polymerization of acrylic acid. The lower peaks at 128 and 125 ppm were assigned to the two carbon species of double bonds ($-CH{=}CH_2$) of acrylic acid which were not completely polymerized in the ATMS-AA after heating at 100 °C for 9 h. The lower resonance peaks at 128 and 125 ppm indicated that a majority of vinyl groups of acrylic acid were polymerized and only a few vinyl groups of acrylic acid existed in the layer structure of ATMS-AA after heating at 100 °C for 9 h. The result of the ^{13}C CP/MAS NMR spectrum of ATMS-AA formed at 100 °C for 9 h indicated that the vinyl groups of acrylic acid in two-dimensional layer space of layered aminopro-

Table 1. Elemental Analytical Results of ATMS-PAA Formed at 100 °C for 24 h

sample	C (wt %)	N (wt %)	S (wt %)	attempted formula
ATMS-PAA	28.71	5.58	0	$CH_2CHCONHCH_2CH_2CH_2$-$SiO_{1.5}$·$4.8H_2O$

pylsilica were not completely polymerized, though all DS was completely displaced by the acrylic acid in the layered structure of layered aminopropylsilica. The reaction time of 9 h at 100 °C apparently was not enough for the polymerization of acrylic acid fixed in layered aminopropylsilica.

Then the reactive precipitates (ATMS-AA) between ATMS-DS and acrylic acid were analyzed using ^{13}C CP/MAS NMR after heating at 100 °C for 24 h. The ^{13}C CP/MAS NMR spectrum of ATMS-AA heated at 100 °C for 24 h showed six resonance peaks at 9.9, 21.5, 34, 42.7, 61, and 178.1 ppm referenced to TMS at 0 ppm (Figure 2c). The resonance peaks at 9.9, 21.5, and 42.7 ppm were assigned to three carbon species from ATMS ($Si-CH_2-CH_2-CH_2-NH_3^+$) in ATMS-AA. The resonance peak at 178.1 ppm was assigned to the carbonyl of amide formed between amino groups of layered aminopropylsilica and carboxyl of acrylic acid. No resonance peaks assigned to vinyl groups of acrylic acid were observed in the ^{13}C CP/MAS NMR spectrum of ATMS-AA after heating at 100 °C for 24 h (Figure 2c), which should be obtained at near 128 ppm as shown in ^{13}C CP/MAS NMR spectrum of ATMS-AA after heating at 100 °C for 9 h (Figure 2b). The resonance peaks at 34 and 61 were assigned to the $-CH_2$ and $-CH$ formed from the polymerization of acrylic acid. The result of the ^{13}C CP/MAS NMR spectrum of ATMS-AA heated at 100 °C for 24 h indicated that the all amino groups of layered aminopropylsilica reacted with the carboxyl of acrylic acid to form amide, the vinyl groups of acrylic acid fixed in the layer structure of layered aminopropylsilica were completely polymerized in ATMS-AA without initiator, and a novel organic−inorganic polymer nanocomposite material named as polyacrylamidepropylsilica (ATMS-PAA) with regular polyacrylamide structure was formed after heating at 100 °C for 24 h.

The elemental analytical results of ATMS-PAA formed at 100 °C for 24 h were shown in Table 1. No S element was observed in the ATMS-PAA. The result of no S element in the ATMS-PAA further indicated that DS in the two-dimensional molecular space of ATMS-DS was completely replaced by the acrylic acid in ATMS-PAA. The elemental analytical results of ATMS-PAA further confirmed that all amino groups in layered ATMS-DS reacted with carboxyl of acrylic acid to form amide.

The powder XRD patterns of ATMS-DS and ATMS-PAA formed at 100 °C for 24 h are shown in Figure 3. The XRD pattern of ATMS-DS exhibits a 001 reflection at $2\theta = 2.2°$ corresponding to interlayer spacing of 4.1 nm in Figure 3a. The layer structure of ATMS-DS is illustrated in Scheme 1b and was discussed previously.[45] The sheet of ATMS-DS has a two-dimensional structure with a Si−O hexagonal network as illustrated in Scheme 1a. The organic groups were alternately arranged on both sides of the silica sheet as illustrated in Scheme 1b. The *d* value (4.1 nm) of the

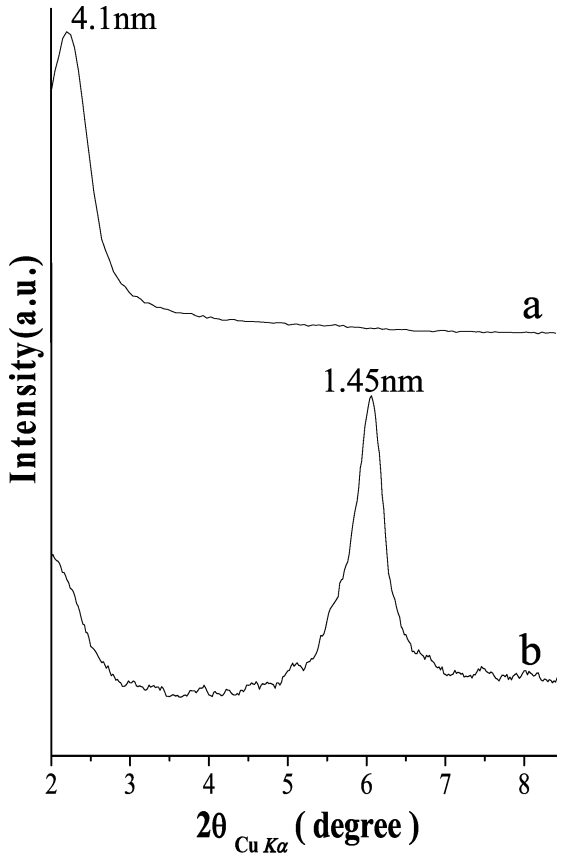
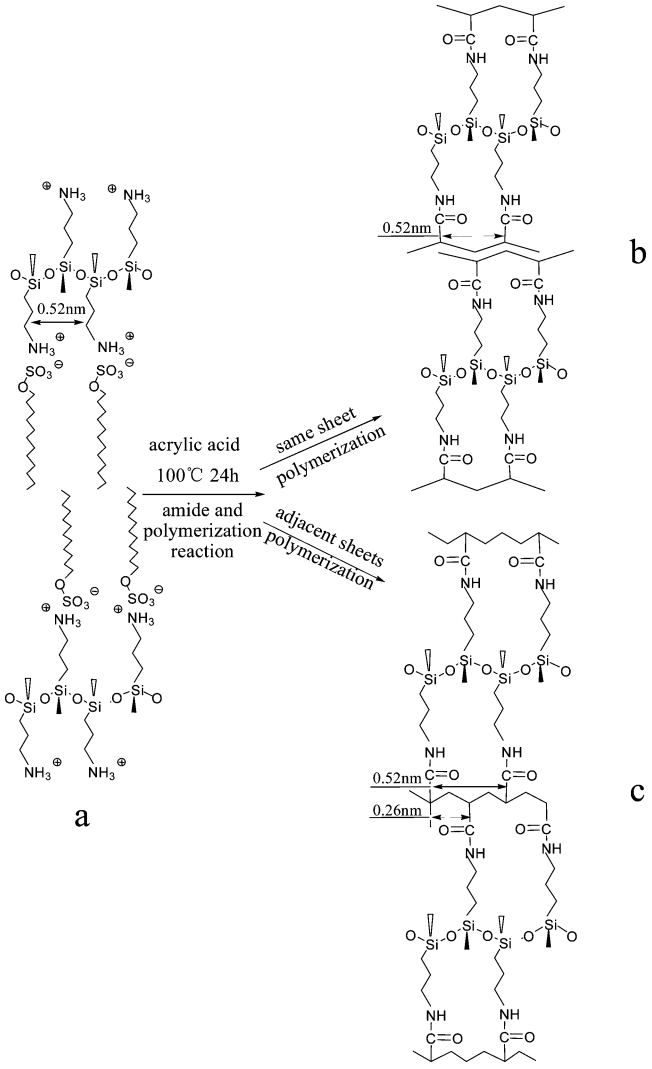


Figure 3. Powder XRD patterns of (a) ATMS-DS and (b) ATMS-PAA formed at 100 °C for 24 h.

reflection peak of ATMS-DS is good agreement with the estimated basal spacing (4 nm) as illustrated in Scheme 1b. The sharp reflection peak indicates the better regularity of the stacking of layers in ATMS-DS. The ATMS-DS is composed of the dodecyl sulfate anion ($C_{12}H_{25}OSO_3^-$:DS) and NH_3^+ $C_3H_6SiO_{1.5}$ in a 1:1 molar ratio.[45] The XRD pattern of ATMS-PAA formed at 100 °C for 24 h exhibits a 001 reflection at $2\theta = 6.1°$ corresponding to interlayer spacing of 1.45 nm (Figure 3b). The better XRD response of ATMS-PAA indicated that the layered aminopropylsilica maintained the stable two-dimensional layer structure as illustrated in Scheme 1a during the polymerization processes of acrylic acid regularly fixed in the layer space of layered aminopropylsilica heated at 100 °C for 24 h. The assignment of the reflection peak will be discussed in the structure model of ATMS-PAA in detail.

According to the results of the IR spectrum, ^{13}C CP/MAS NMR spectrum, elemental analysis, and XRD pattern of ATMS-PAA formed at 100 °C for 24 h, the DS was completely replaced by acrylic acid in the two-dimensional molecular space of ATMS-PAA. The all amino groups reacted with carboxyl of acrylic acid to form amide in layer structure of layered aminopropylsilica. The acrylic acid was fixed in the layer structure of layered aminopropylsilica through the formation of amide between amino groups of layered aminopropylsilica and carboxyl of acrylic acid. The vinyl groups of acrylic acid were completely polymerized in ATMS-PAA without initiator after heating at 100 °C for 24 h. The fact of complete polymerization of acrylic acid fixed in the narrow nanospace of layered aminopropylsilica

Scheme 2. Possible Regular Polymeric Structure of Acrylic Acid Fixed in Two-Dimensional Molecular Space of Layered ATMS-PAA[a]



[a] (a) ATMS-DS, (b) polymerization in the same sheet (bilayers), and (c) polymerization in the adjacent sheets (monolayers).

indicates that the polymeric structure of acrylic acid fixed in layered aminopropylsilica must be very regular, because any irregular polymeric structure will induce incomplete polymerization of acrylic acid fixed in narrow nanospace of layered aminopropylsilica. Otherwise, better XRD respond was obtained from ATMS-PAA heated at 100 °C for 24 h (Figure 3b). The sharp XRD pattern also indicates that the polymeric structure of acrylic acid regularly fixed in the layer space of layered aminopropylsilica must be regular, because any irregular polymeric structure of acrylic acid fixed in layer space of layered aminopropylsilica will broaden the XRD reflection peak of ATMS-PAA.

The possible regular polymeric structure of acrylic acid fixed in two-dimensional molecular space of layered ATMS-PAA formed at 100 °C for 24 h is illustrated in Scheme 2. The first possible regular polymeric structure of polyacrylamide fixed in layered aminopropylsilica had acrylamide molecules polymerized on the same side of one sheet to form bilayers of polyacrylamide in layered ATMS-PAA as illustrated in Scheme 2b. The second possible regular polymeric structure of polyacrylamide fixed in layered aminopropylsilica had acrylamide molecules polymerized in adjacent sheets to form monolayers of polyacrylamide in layered ATMS-PAA as illustrated in Scheme 2c. The distance between acrylamide molecules fixed on the same side of one sheet of layered aminopropylsilica is about 0.52 nm, because the organic groups were alternately arranged on both sides of the silica sheet of layered aminopropylsilica.[45,46] If the polymerization occurred between acrylamide molecules on the same side of one sheet of layered aminopropylsilica to form bilayers of polyacrylamide in layered ATMS-PAA, the alkyl chain between acrylamide molecules fixed on the same side of one sheet of layered aminopropylsilica should contain three carbon atoms as illustrated in Scheme 2b. The distance of 0.52 nm between acrylamide molecules fixed on the same side of one sheet of layered aminopropylsilica is apparently too far for the length of a three carbon atom chain (about 0.25 nm). Thus, it is hardly considered that polymerization had taken place between acrylamide molecules fixed on the same side of one sheet of layered aminopropylsilica to form bilayers of polyacrylamide in layered ATMS-PAA as shown in Scheme 2b.

If the polymerization occurred between acrylamide molecules fixed in adjacent sheets of layered aminopropylsilica to form monolayers of polyacrylamide in layered ATMS-PAA, the alkyl chain between acrylamide molecules fixed on the same side of one sheet of layered aminopropylsilica should contain five carbon atoms as illustrated in Scheme 2c. The distance of 0.52 nm between acrylamide molecules fixed on the same side of one sheet of layered aminopropylsilica apparently agreed with the length of a five carbon atom chain (about 0.5 nm). Otherwise, the alkyl chain between acrylamide molecules fixed in adjacent sheets of layered aminopropylsilica contains three carbon atoms, when the monolayers of polyacrylamide are formed in layered ATMS-PAA as illustrated in Scheme 2c. The length of a three carbon atom chain (about 0.25 nm) is in agreement with the distance between acrylamide molecules fixed in adjacent sheets (about 0.26 nm) of layered aminopropylsilica. Therefore, the most possible polymeric structure of acrylamide molecules fixed in the layer structure of layered aminopropylsilica is that acrylamide molecules were polymerized in adjacent sheets to form monolayers of polyacrylamide in layered ATMS-PAA as illustrated in Scheme 2c. According to the structure model shown in Scheme 2c, the distance between silica layers is estimated to be about 1.5 nm. The *d* value (1.45 nm) of the XRD reflection peak of ATMS-PAA formed at 100 °C for 24 h (Figure 3b) is in good agreement with the estimated distance (1.5 nm) between silica layers as shown in Scheme 2c.

The reaction solution (filtrate) was analyzed using ^{13}C NMR after heating for 24 h at 100 °C. The ^{13}C NMR spectrum of the reaction solution showed nine peaks at 33.51, 59.67, 127.88, 127.93, 131.39, 133.08, 166.12, 171.69, and 177.11 ppm (Figure 4). The peaks at 127.93, 133.08, and 171.69 ppm were assigned to the carbon species of double bonds and carboxyl of unreacted acrylic acid, respectively. The peaks at 33.51, 59.67, and 177.11 ppm were assigned to the $-CH_2$, $-CH$, and carbon species of carboxyl of poly-

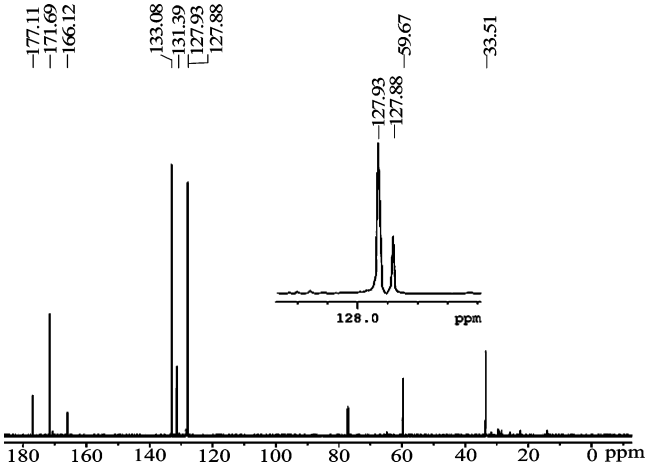


Figure 4. ^{13}C NMR spectrum of reaction solution of ATMS-PAA after heating at 100 °C for 24 h.

(acrylic acid), respectively. The peaks at 127.88, 131.39, and 166.12 ppm were considered to be assigned to the carbon species of vinyl groups and carbonyl due to formation of acid anhydride during heating 24 h at 100 °C in an acrylic acid reaction solution, respectively. A series of lower peaks near 30 ppm were considered to be due to the DS in the layer space of layered ATMS-DS, displaced by acrylic acid and dissolved in the pure acrylic acid solution. It is known that much of the acrylic acid was not polymerized in reaction solution without initiator from the result of the ^{13}C NMR spectrum of the reaction solution of acrylic acid even after heating at 100 °C for 24 h (Figure 4). The difference between the two-dimensional molecular space with regular amino groups in structure and free space for the polymerization of acrylic acid was confirmed. The acrylic acid was completely polymerized in layered ATMS-PAA without initiator after heating at 100 °C for 24 h. The polymerization of acrylic acid fixed in two-dimensional molecular spaces of layered aminopropylsilica was apparently easier than in free space. However, when acrylic acid was fixed in the two-dimensional molecular space of layered aminopropylsilica, the distance between double bonds of acrylic acid approached 0.25 nm in adjacent layer structures as shown in Scheme 2c. The double bonds of acrylic acid which were fixed in such a close distance are very prone to be polymerized after heating at 100 °C. The polymerization of acrylic acid was facilitated in the two-dimensional molecular space with regular amino groups compared with free space. The two-dimensional molecular space of layered aminopropylsilica with regular amino groups showed a potential of influencing molecular reaction processes.

Conclusion

In this research, acrylic acid was used to investigate the capabilities of two-dimensional molecular space of layered aminopropylsilica with regular amino groups on influencing and controlling molecular reaction processes. The acrylic acid was regularly fixed in the layer structure of layered aminopropylsilica through the formation of amide between carboxyl of acrylic acid and amino groups of layered aminopropylsilica after heating at 100 °C. The acrylic acid regularly fixed in the layer structure was completely polymerized to form a novel organic−inorganic nanocomposite material (layered polyacrylamidepropylsilica, ATMS-PAA) with monolayers of polyacrylamide in layer space of layered aminopropylsilica without initiator after heating 24 h at 100 °C. The polymerization of acrylic acid regularly fixed in layered aminopropylsilica was facilitated in the two-dimensional molecular space with regular amino groups compared with free space. The distance between acrylic acid molecules regularly fixed in the layer structure of layered aminopropylsilica was considered to be a key point for facilitating the polymerization of vinyl groups and deciding the polymeric structure of layered ATMS-PAA. These results indicate that the two-dimensional molecular space materials with regular functional organic groups in structure are promising materials for influencing and controlling molecular reaction processes by utilization of the interaction between the regular functional groups in two-dimensional structure and guest molecules. Otherwise, the novel organic−inorganic nanocomposite materials such as layered polyacrylamidepropylsilica are also interesting for the research of nanocomposite materials.

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